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FORMATION METHOD FOR POLYCRYSTALLINE SEMICONDUCTOR FILM

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circuit is used or the integrated circuit is connected to manufacture a semiconductor device, the fabrication process becomes very complex, and each process has a great influence on the yield of the product. Particularly, when a new film is formed by the gas phase method, there is a tendency for degradation or damage to be generated in one part already formed within the substrate under the film formation surface by the heating that is required for said chemical reaction; thus, there is a great need to form the film at as low a temperature as possible and for the formed film to be dense and chemically stable. In particular, when the substrate with the film formation surface is a silicon semiconductor (an intrinsic semiconductor in essence with a specific resistance of 500 Ωcm or greater) and the monocrystalline substrate is heated at a high temperature in order to produce a p- or n-type semiconductor layer on it by vapor deposition, there are cases in which a thermal conversion occurs in the substrate and a change occurs from intrinsic property to an n-type specific resistance of a few tens of Ωcm. Therefore, it was very important industrially to form a polycrystalline semiconductor film on the film formation surface of the substrate at a low substrate heating temperature of 900°C or less.

Gas phase methods are generally separated into the gas phase deposition method of forming a polycrystalline film at a low temperature of 400-900°C and the gas phase growth method of forming a monocrystalline film on a monocrystalline substrate at 900-1,100°C when forming, for example, as a silicon semiconductor film. The present invention relates to a gas phase

method, in particular, the former formation method for polycrystalline semiconductor film.

The main objective of the present invention is to achieve film formation at a low temperature of 400-750°C at which degradation of the electrical characteristics of the substrate does not occur and for the crystal grain of the formed film to be small, 0.01-1 μm, when a polycrystalline semiconductor film is formed by the gas phase method, for example, when a polycrystalline film of silicon semiconductor is formed; namely, to form a dense film. The present invention achieved an improvement in the film formation, density, and uniformity in the film formed on the film formation surface at said low temperature as well compared to the conventional technology by forming or growing a film on the film formation surface under reduced pressure. In addition, by reducing the quantity of aria [sic; carrier] gas used when introducing the reaction gas into the reaction furnace (chamber) by maintaining the reaction system at a reduced pressure in the present invention below that used in the conventional technology so that transmission of the thermal energy of the heated substrate to the reaction gas is accelerated along with causing chemical activation in the reaction gas with the catalyst provided at a position separated from the film formation surface prior to decomposing the reaction at on or near the film formation surface, growth of the film on the film formation surface is assisted, and film formation at a low temperature is promoted. The present invention is characterized by the fact that said operations are carried out within a reaction chamber maintained under reduced pressure. As a result, the mean free path of the reaction gas increases under

decompression, and the impact energy of the reaction gas on the film formation surface becomes great; thus, there is the merit that the formed film is made dense with minimal lattice defects; namely, the polycrystalline grains in the polycrystalline film are made small, and a film of minimal grain boundary influence can be produced.

As apparent from said explanation, it is clear that the present invention is different from the method based on the conventional concept, namely, the method of diluting the reaction gas with a carrier gas of hydrogen, etc., introducing it into a reaction chamber maintained under atmospheric pressure state of the hour, and carrying out film formation using a catalyst. As an application [sic], it is very effective for the formation of fine patterns, [the prevention of] abnormal diffusion, etc., when applied as a lead in a semiconductor device. Below, an explanation will be given according to an application example.

As the reaction gas, a silicide compound gas such as silane, dichlorosilane, or silicon tetrachloride was used. In the explanation below, an example of using silane, which is easy to handle, will be discussed. As the material with the film formation surface for the film, a publicly known monocrystalline silicon semiconductor wafer or a substrate exposed to a monocrystal or amorphous insulation material, for example, silicon oxide, silicon nitride, or arushia [transliteration] on which at least the film formation surface was used in this application example.

The gas phase method of the present invention is classified into a gas phase growth method in which a monocrystalline film is formed, and a gas phase reaction method, in which a

polycrystalline film is formed. Particularly, when a film of the same material is grown on a monocrystalline substrate, it is generally called epitaxial growth, and the reaction gas is diluted with a carrier gas and then grown on a substrate heated to a high temperature by introducing it into the reaction chamber. When this heating temperature is 400-900°C, the minimum temperature at which a polycrystalline film is formed and epitaxial growth occurs is 900°C. Moreover, when the amount of the carrier gas used in said growth is minimized, low-temperature growth becomes possible, but the growth rate of the film with respect to said composite temperature shifts to the low temperature side when compared with the normally obtained curve at which polycrystalline film is formed at 1,000°C or less, and epitaxial growth is executed at a temperature of 1,000°C or higher, as in curve C of Figure 1. Namely, curve C, at which film formation is possible even at a low temperature (1,400-750°C [i.e. 400-750°C]), silane is diluted with argon, but the concentration is 3.0%. As the concentration of silane with respect to the carrier gas increases, it is found that the temperature of the chamber at which film formation is possible shifts in the direction of low temperature. Also, when an epitaxially grown film is grown at a high temperature of about 1,000°C using a high concentration of silane gas, the crystallinity becomes unfavorable, and when a high concentration of gas of 5.0% or greater is used, an annular diffraction image indicating a polycrystalline structure locally in the film is observed when observed by the electron diffraction methods. In the device used in the present invention, a heater formed into a coil by winding [illegible] m [meters] of heater of Kanthal or dichromium No. 1 (0.7

on an insulator was designed to prevent diffusion of heat to the periphery by surrounding all but the film formation substrate with transparent quartz, opaque quartz, stainless steel plate (SUS 32), and quartz wool, and producing a reaction chamber in which a surface reaction can be carried out by heating at a range from room temperature to 1,100°C. If a space reaction were to occur in the silane were to decompose in space, lumped silane clusters would be formed; thus, the formed film would become a polycrystalline without fail, even if the temperature of the film formation surface were 1,000°C or greater. A so-called dense film structure thus cannot be obtained due to generation of voids at the boundaries between the clusters, namely, at the crystal grain boundaries, and there is a tendency of forming an unfavorable polycrystalline film due to generating many torafugu [transliteration] at the grain boundary. Of course, when polycrystalline film is formed on a polycrystalline or amorphous insulation material (e.g., silicon oxide, silicon nitride, or aluminum film) substrate surface, the concentration of the reaction gas within the reaction chamber can be high. It is then possible to cause a space reaction. However, in said film growth method, the uniformity of the film is not within ±3%, and it is necessary to maintain the reaction chamber of the present invention under reduced pressure, as will be discussed below. Namely, in the method of the present invention, the reaction chamber with the film formation surface installed is evacuated in order to improve the uniformity of the low-temperature film formation. The pressure of this reaction chamber was changed to 1 torr from atmospheric pressure, but the thickness of the obtained film was the greatest at atmospheric pressure, and the

[illegible]wth rate decreased as the pressure decreased. However, when [illegible] formed film is put to use, uniformity of the film is very important. Whereas there was a variance in said uniformity of ±5% [illegible] a film formed at atmospheric pressure, it was found that the [illegible]formity of the film formed under a reduced pressure of, for [illegible]ample, 100 torr was superior to ±1%. As a result of having [illegible]ced the amount of carrier gas used within the reaction [illegible]stem, curve C as shown in Figure 1 is obtained under [illegible]spheric pressure, but when the reaction system was placed [illegible] a reduced pressure of [illegible] torr, curve B or, [illegible]pectively, A is obtained. At 1.0 torr or less, the film growth [illegible] becomes low, equal to essentially no film formation, but on [illegible] other hand, the film uniformity was the worst, about ±5%, at [illegible]spheric pressure, was ±2-3% at 300 torr, and was within ±1% [illegible]00 torr. Namely, the uniformity of the film becomes more [illegible]rable in the gas phase method in which the reaction (chamber) [illegible]intained at a more highly reduced pressure, and electron [illegible]scopic defects decreased. It was also found that this is due [illegible] increase in the mean free path of the reaction material; [illegible] it is identical to high-temperature film formation.

[illegible]imentally, it was found regarding the formation of [illegible]crystalline semiconductor film using silane that the use of a [illegible]sure in the range of 10-500 torr is suited for practical use [illegible] formation temperature in the range of 400-900°C and a [illegible]ntration in the range of 1.0-0.3% [Si/C]. As a result, when a [illegible]crystalline silicon semiconductor film is formed at a [illegible]ness of 1 μm at a film formation surface temperature of, for [illegible]ple, 650°C, the crystal grain size of the film formed is 5-30 [illegible]th atmospheric pressure at 760 torr, within the reaction

system. Under these conditions, the grain boundary was multidimensional, and there was a variance in the film thickness of ±10%. On the other hand, when the pressure within the reaction system was reduced to 50~100 torr, the crystal grain size of the polycrystalline in the formed film was very small, 0.01~0.1 μm, and it was found from the result of electron diffraction measurement that an amorphous film was formed; thus, it was possible to obtain a film of high film thickness uniformity without abnormal diffusion at the crystal grain boundary even when an impurity was doped in said semiconductor. As noted above, it was found that forming a polycrystalline film under reduced pressure has a noticeable effect industrially which could not be conceived from simple deduction.

In said application example, the system was arranged vertically, and the flow rate of the silane was varied in a range of 5~20 cc/min, but only the scale of the vertical coordinates in figure 1 changed with regard to the crystals. A claim can be made that the horizontal arrangement is superior for mass production.

Furthermore, in the present invention, a catalyst was provided at a position separated from the film formation surface in order to improve the uniformity of the formed amorphous film and to reduce the temperature. The reaction gas was chemically activated by said catalyst. This chemical activation made possible a film growth rate identical to that of the conventional technology at a temperature 50°C lower than that of the conventional technology. In this application example, a catalyst comprising gas-permeable metal, such as platinum, titanium, etc., in multiple layers and including a granular catalyst of zinc oxide, copper oxide, zinc, or nickel oxide inserted in a

[illegible]500-grain catalytic column was used. The catalyst was provided [illegible] a distance of 5-50 cm from the film formation surface and was designed for the reactive gas to pass through the column. Before use, said catalyst was reduced in hydrogen at the necessary temperature for chemical activation. For example, copper oxide and zinc were reduced for about 2 h in hydrogen at 200°C.

Said chemical activation process not only has the merit of forming the film at a low temperature but also can improve the uniformity of the formed film.

In a relatively thin gas phase grown film (thickness of 2 μm or less) in particular, it was found that there is a function of making the film uniform and the distribution of the donor and acceptor impurity injected according to the gas and functioning as an impurity such as phosphine, teiborane [sic; diborane], etc. within the film uniform.

Said application example was discussed only regarding a case using silane, but, needless to say, the technological concept is absolutely the same even when germanium hydride, germanium chloride, and other germanium halides are used.

As apparent from the explanation above, the gas phase deposition method for forming a polycrystalline semiconductor film according to the present invention has a noticeable effect for the semiconductor industry, the merit becomes effective when forming a thin film in particular, and the contribution to the semiconductor industry is considerable.

Claims

1. A formation method for polycrystalline semiconductor film, characterized by the fact that a polycrystalline silicon or germanium film is formed on a film formation surface by introducing a reaction gas of silicon or germanium into a reaction system maintained under reduced pressure and causing a chemical reaction.

2. A formation method for polycrystalline semiconductor film described in Claim 1, characterized by the fact that a catalyst is installed at a position separated from the film formation surface and the reaction gas is activated chemically.

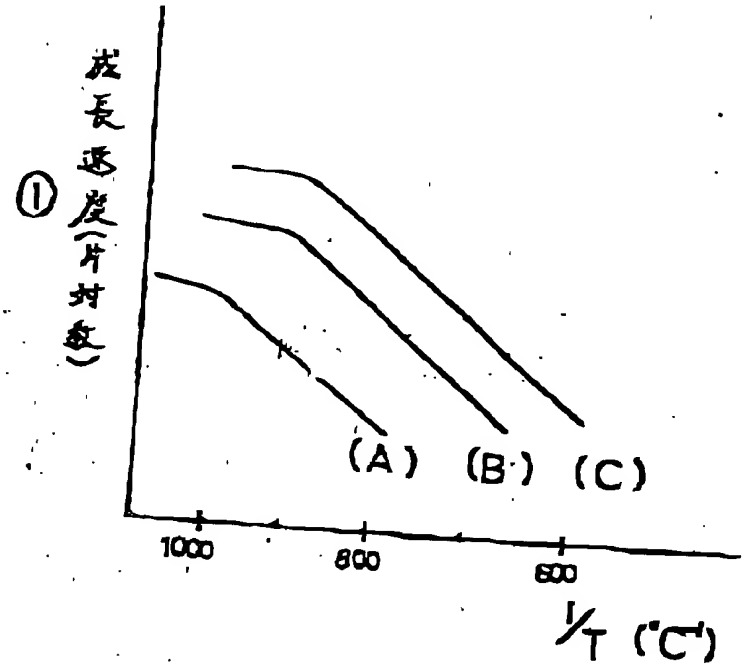

Figure 1
Growth rate (semilogarithm)